PATENT ABSTRACTS OF JAPAN

(11)Publication number : **2000-327339**

(43)Date of publication of application : **28.11.2000**

(51)Int.CI. C01G 51/00
H01M 4/02
H01M 4/58
H01M 10/40

(21)Application number : **11-136360**

(22)Date of filing : **17.05.1999**

(71)Applicant : **MITSUBISHI CABLE IND LTD**

(72)Inventor : **GOSHO ITARU**

(54) Li-Co-BASED COMPOUND OXIDE AND ITS PRODUCTION

(57)Abstract:
PROBLEM TO BE SOLVED: To produce an Li-Co-based compound oxide useful as a positive pole active material for a nonaqueous electrolyte battery such as a lithium secondary battery and capable of improving charge and discharge cycle characteristics of the battery and to provide a method for producing the Li-Co-based compound oxide.
SOLUTION: This particulate Li-Co-based compound oxide has the sum value A (μm) of respective lattice spacings in (104), (105), (009), (107), (108) and (113) indices of planes, the specific surface area B (m2/g) and the average particle diameter C (μm) satisfying the following formula: formula: $0.025 \leq [(A-11)/(B.C)] \leq 0.04$. The method for producing the Li-Co-based compound oxide comprises carrying out water washing treatment of a particulate material of the Li-Co-based compound oxide, regulating the amount of water-soluble lithium compound-based impurities to ≤ 0.05 wt.% and then heat-treating the resultant compound oxide at 400-700°C for 0.5-50 h. The Li-Co-based compound oxide is suitable for producing a long-lived lithium secondary battery for various kinds of electrical equipment, especially for portable articles, etc.

LEGAL STATUS

[Date of request for examination]	28.06.2001
[Date of sending the examiner's decision of rejection]	
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	

[Date of final disposal for application]	
[Patent number]	3308232
[Date of registration]	17.05.2002
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

CLAIMS

[Claim(s)]
[Claim 1] The Li-Co system multiple oxide characterized by the total value A (micrometer), the specific surface area B (m2 / g), and mean particle diameter C (micrometer) of indices of crystal plane (104), (105), (009), (107), (108), and (113) each lattice spacing that can be set being the granular object with which are satisfied of a bottom type.
0.025 <=[(A-11) /(B-C)] <=0.04 -- [Claim 2] A granular object is a Li-Co system multiple oxide according to claim 1 whose specific surface area B is 0.1-0.3m2 / g and whose mean particle diameter C is 10-25 micrometers.
[Claim 3] For a granular object, the amount of a water-soluble lithium compound system impurity is Li2 CO3 about this impurity. Li-Co system multiple oxide according to claim 1 or 2 which it converts into an amount and is 0.05 or less % of the weight.
[Claim 4] The Li-Co system multiple oxide according to claim 1 to 3 which is an object for the positive active material of a nonaqueous electrolyte rechargeable battery.
[Claim 5] Rinsing processing of the granular object of a Li-Co system multiple oxide is carried out, and the amount of a water-soluble lithium compound system impurity is Li2 CO3 about this impurity. The manufacture approach of a Li-Co system multiple oxide given in either of claims 1, 3, and 4 characterized by converting into an amount, making it become 0.05 or less % of the weight, and subsequently heat-treating under 400-700-degree C high temperature in air or an inert atmosphere for 0.5 to 50 hours.
[Claim 6] The manufacture approach of a Li-Co system multiple oxide according to claim 5 that mean particle diameter C carries out rinsing processing, and subsequently heat-treats the granular object which is 10-25 micrometers.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to a Li-Co system multiple oxide useful as positive active material of nonaqueous electrolyte rechargeable batteries, such as a lithium secondary battery, and its manufacture approach especially about a Li-Co system multiple oxide and its manufacture approach.
[0002]
[Description of the Prior Art] Those parts have come [as positive active material of current and a lithium secondary battery, / the Li-Mn system multiple oxide, the Li-nickel system multiple oxide, the Li-Co system multiple oxide, etc. were proposed, and] to be used. Among those, since a Li-Mn system multiple oxide and a Li-nickel system multiple oxide are abundant in the resources of Mn or nickel, while it can manufacture cheaply, a Li-Mn system multiple oxide has the problem which cannot manufacture the rechargeable battery of high capacity easily generally, and on the other hand, a Li-nickel system multiple oxide is chemically unstable, and has a problem in respect of the safety of a rechargeable battery. On the other hand, since the Li-Co system multiple oxide is chemically stable as compared with a Li-nickel system multiple oxide, it is easy handling,

and since it can moreover manufacture the rechargeable battery of high capacity, practical use is presented with them by current. [most]

[0003] To the rechargeable battery using the Li-Co system multiple oxide which has this advantage, the demand which improves the cell property further is increasing, and the proposal and report for it are also made recently. For example, in JP,7-118318,B, it is LiCoO2. In manufacturing, it blends and mixes and the use rate of a raw material slack lithium compound and a cobalt compound is heated so that a lithium may become rich, and if it carries out, carrying out rinsing removal of the unreacted lithium compound contained in a resultant or the byproduction **** lithium carbonate, the thing which write and which the discharge capacity of a rechargeable battery improves are indicated. Moreover, it is LiCoO2 in order to prevent beforehand the explosion accident based on the unusual cell reaction under operation of a cell in JP,5-182667,A. Making a lithium carbonate living together and its concrete approach are indicated.

[0004] By the way, when the Li-Co system multiple oxide formed by the granular object which has the specific crystal structure and has a specific specific surface area and particle size from the latest research which this invention person did was used as positive active material, it became clear that the charge-and-discharge cycle property of a lithium secondary battery could be improved.

[0005]

[Problem(s) to be Solved by the Invention] Carrying out a deer, it develops and completes based on the above-mentioned new knowledge, and this invention is useful as positive active material of nonaqueous electrolyte rechargeable batteries, such as a lithium secondary battery, and makes it a technical problem to offer the Li-Co system multiple oxide which can improve the charge-and-discharge cycle property of this cell, and its manufacture approach.

[0006]

[Means for Solving the Problem] The above-mentioned technical problem is solvable by a following Li-Co system multiple oxide and its following manufacture approach.

** The Li-Co system multiple oxide characterized by the total value A (micrometer), the specific surface area B (m2 / g), and mean particle diameter C (micrometer) of indices of crystal plane (104), (105), (009), (107), (108), and (113) each lattice spacing that can be set being the granular object with which are satisfied of a bottom type (1).

0.025 <=[(A-11) /(B-C)] <=0.04 (1)

** A granular object is a Li-Co system multiple oxide given [the given specific surface area B is 0.1-0.3m2 / g / above-mentioned] in ** the given mean particle diameter C is 10-25 micrometers.

** For a granular object, the amount of a water-soluble lithium compound system impurity is Li2 CO3 about this impurity. The above-mentioned ** which it converts into an amount and is 0.05 or less % of the weight, or Li-Co system multiple oxide given in **.

** A Li-Co system multiple oxide given in either the above-mentioned ** which is an object for the positive active material of a nonaqueous electrolyte rechargeable battery - **.

** Carry out rinsing processing of the granular object of a Li-Co system multiple oxide, and the amount of a water-soluble lithium compound system impurity is Li2 CO3 about this impurity. The manufacture approach of a Li-Co system multiple oxide given in the

above-mentioned ** characterized by converting into an amount, making it become 0.05 or less % of the weight, and subsequently heat-treating under 400-700-degree C high temperature in air or an inert atmosphere for 0.5 to 50 hours, **, or **.
** The manufacture approach of a Li-Co system multiple oxide given [above-mentioned] in ** that mean particle diameter C carries out rinsing processing, and subsequently heat-treats the granular object which is 10-25 micrometers.
[0007]
[Embodiment of the Invention] The Li-Co system multiple oxide of this invention is LiCoO2 in chemical structure. Or it may be shown by what [what permuted a part of the Co by a kind or two sorts or more of other elements] (2), for example, the following general formula.
LiA Co1-X Mex O2 (2)
a general formula (2) -- setting -- A -- 0.05-1.5 -- it is 0.1-1.1 preferably and, as for X, it is desirable 0.01 to 0.5 and that it is especially 0.02-0.2. As an element Me, 3 - 10 group element of a new periodic table, for example, Zr, V, Cr, Mo, Mn, Fe, nickel, etc., is 13 or - 15 group element, for example, B, aluminum, germanium, Pb, Sn, Sb, etc. If it is in the Li-Co system multiple oxide which permuted Co by two or more sorts of those elements, the total quantity of two or more sorts of elements should just be within the limits of Above X.
[0008] The Li-Co system multiple oxide of this invention is formed by the granular object with which the total value A (micrometer), the specific surface area B (m2 / g), and mean particle diameter C (micrometer) of indices of crystal plane (104), (105), (009), (107), (108), and (113) each lattice spacing (d value) that can be set are satisfied of a formula (1). When the value of [(A-11) /(B-C)] in this formula uses the granular object which is size as positive active material from less than 0.025 and 0.04, especially the Li-Co system multiple oxide that it both comes to form by the granular object with which amelioration good in the charge-and-discharge cycle property of a lithium secondary battery is not found, but a deer is carried out, and it is satisfied of a bottom type (3) in this invention is desirable.
0.032 <=[(A-11) /(B-C)] <=0.038 (3)
[0009] As long as a formula (1) is satisfied, the Li-Co system multiple oxide of this invention does not have especially a limit from a viewpoint of the charge-and-discharge cycle property of a lithium secondary battery about each magnitude of the total value of d value, specific surface area, and mean particle diameter. However, when too little [the total value of d value], the compressive strain of a under [a crystal] are large, and since it is in the inclination for the tension distortion in a crystal to be large when it is excessive, and to carry out the deer, and for the case of a gap to make the charge-and-discharge cycle property of a cell fall, on the other hand, it is not desirable. Therefore, as for this especially total value, 11.11 to about 11.14 are [11.10 to about 11.15] desirable. Moreover, since too little [mean particle diameter] Li-Co system multiple oxide is rich in reactivity, and it is easy to cause an unusual cell reaction generally, and electric resistance is large, for this reason the Li-Co system multiple oxide with excessive it leads to reduction of the energy density per unit volume of a lithium secondary battery on the other hand, especially mean particle diameter has desirable about 15-20 micrometers about 10-25 micrometers. The range where the specific surface area of a Li-Co system multiple oxide is desirable is 0.1-0.3m2 / g grade from a viewpoint of the charge-and-

discharge cycle property of a lithium secondary battery, especially 0.15-0.25m2 / g grade.
[0010] In this invention, the total value of d value of the granular object of a Li-Co system multiple oxide, specific surface area, and mean particle diameter can be measured by the approach shown below, respectively.
[Measurement of the total value of d value] Using copper X-ray diffractometer, an anticathode measures indices of crystal plane (104), (105), (009), (107), (108), and each d value that reaches (113) by the conditions and approach of divergent slit 0.5deg., scattering slit 0.5deg., and light-receiving slit 0.15mm, step size 0.006deg., and the step scan for measurement time amount 0.5 seconds, and computes the total value (micrometer) of these d value.
[Measuring method of specific surface area] Nitrogen is twisted by the gas-phase-adsorption method (one point method for BET method) made into adsorbent among the adsorption processes indicated by 178th page - the 184th page of "the ingredient chemistry [Yasuo Arai work, the 9th ** of the first edition, the Baifukan (Tokyo) issue, and 1995] of fine particles."
[Measuring method of mean particle diameter] The granular object of a Li-Co system multiple oxide is fed into organic liquids, such as water or ethanol. The dispersion liquid which carried out distributed processing for about 2 minutes and which were obtained where an about 35-40kHz supersonic wave is given are used. And the amount of the granular object in that case is made into the amount from which the laser permeability (ratio of the output quantity of light to the amount of incident light) of these dispersion liquid becomes 70 - 95%. subsequently, these dispersion liquid -- taking the post -- a micro truck grading-analysis meter -- applying -- dispersion of laser light -- the particle size (D1 --) of each granular object D2, D3 .., and the existence number (N1, N2, N3 ...) for every particle size are measured (according to the micro truck grading-analysis meter in the particle size (D) of each granular object, a spherical equivalent diameter is automatically measured for every granular object of various configurations.). . A deer is carried out and mean particle diameter (micrometer) is computed by the bottom formula (4) from the number (N) of each particle and each particle size (D) which exist in a visual field.
Mean-particle-diameter (micrometer) = (sigmaND3 / sigmaN) 1/3 (4)
[0011] Below, the manufacture approach of the granular object of the Li-Co system multiple oxide of this invention is explained. Generally the granular object of a Li-Co system multiple oxide As a start raw material, the oxide of a lithium or cobalt, a hydroxide, a halogenide, A nitrate, an oxalate, a carbonate, etc. are used. The mixture of this lithium compound and cobalt compound Or when a part of Co as shown by the formula (2) manufactures the Li-Co system multiple oxide permuted by other elements, the mixture which carried out little combination of the compound of a permutation element is made to react to the above-mentioned mixture by the well-known approach. For example, heating baking of this mixture is carried out around 1000 degrees C in atmospheric air for 1 to 50 hours. The massive object of the Li-Co system multiple oxide manufactured in this way is ground, selection extraction can be carried out and the granular object which has the total value of d value with which it classifies if needed and a formula (1) is filled, specific surface area, and mean particle diameter can be obtained. Above all, it is Li2 CO3 at the after-mentioned formula (5) about the amount of a water-soluble lithium compound system impurity by rinsing processing etc. in the reason for

carrying out a postscript. What becomes as 0.05 or less % of the weight with the value converted into the amount is desirable. In addition, it is Li2 CO3 according [on the following or / the amount of a water-soluble lithium compound system impurity] to a formula (5). The amount of conversions shall be meant. Moreover, the granular object of the Li-Co system multiple oxide of this invention The granular object of Li-Co system multiple oxides, such as what ground and obtained the above-mentioned massive object, Carry out the postscript of the granular object with a mean particle diameter of 10 micrometers - 25 micrometers above all, and rinsing processing is carried out. After drying if needed, at 400-700 degrees C in atmospheric air or inert gas ambient atmospheres, such as nitrogen and an argon, especially for 0.5 to 50 hours About 1 - 20 hours, It can manufacture especially preferably for 0.5 to 50 hours also by heat-treating at 500-700 degrees C for about 1 to 20 hours. In addition, since a lithium carbonate will arise and it will lead to increase of the content of an impurity if carbon dioxide gas exists in the ambient atmosphere which heat-treats, as for the carbon dioxide partial pressure in an ambient atmosphere, it is desirable to be referred to as 10 or less mmHgs.

[0012] general -- the mixing ratio of a lithium compound and a cobalt compound -- from the reasons nil why the fugacity of a rate according [a lithium compound] to evaporation as compared with a cobalt compound is high etc. -- usually -- a lithium -- it is made to become rich Consequently, the obtained Li-Co system multiple oxide which carried out heating baking contains lithium compound system impurities, such as lithium oxide, a lithium hydroxide, and a lithium carbonate, in many cases.

[0013] this invention -- setting -- this lithium compound system impurity, if water-soluble lithium compound system impurities, such as a lithium hydroxide and a lithium carbonate, are removed above all so that the amount in the inside of a granular object may become 0.05 or less % of the weight by rinsing processing If the rinsing processing object from which the water-soluble impurity to write was removed much more preferably is heat-treated on condition that the above, the effectiveness that whose manufacture yield of the granular object which fills a formula (1) or a formula (3) improves, and the charge-and-discharge cycle property of a lithium secondary battery moreover improves will also become large. Since a water-soluble lithium compound system impurity also has the problem which corrodes this charge collector and falls the charge-and-discharge cycle property of a rechargeable battery when a charge collector is furthermore a product made from aluminum, reduction of a water-soluble lithium compound system impurity is desirable also from this field. This rinsing processing can be performed by the usual approach of giving mechanical agitation and a supersonic wave if needed in the case of processing, using distilled water and ion exchange water as wash water. In addition, the quantum of the amount D of lithium compound system impurities (Li2 CO3 the amount of conversions) which remains in the granular object by which rinsing processing was carried out can be carried out by a following approach and a following formula (5).

The [quantum approach of the water-soluble lithium compound system impurity D] After making about 10g of the granular object of a Li-Co system multiple oxide suspend in 100ml of pure water and agitating it for 10 minutes, it carries out a ** exception, and it titrates with a 0.1-N hydrochloric acid about the filtrate, Li ion concentration L (a mol/liter) is computed from the drip of this hydrochloric acid, and the water-soluble lithium compound system impurity D (% of the weight) is computed by the bottom

formula (5).
D=Lx(molecular weight of Li2 CO3: 73.89) /2=36.95L (5)
[0014] According to research of this invention person, it becomes easy to obtain the granular object which the total value and specific surface area of d value change although the granular object of a Li-Co system multiple oxide does not change with above-mentioned rinsing processings or heat treatments and especially the mean particle diameter does not change with rinsing processing and heat treatments substantially like ** generally, consequently fills a formula (1) and a formula (3).
[0015] The Li-Co system multiple oxide of this invention can be used as positive active material of nonaqueous electrolyte cells, such as a lithium secondary battery, for example, can be used with other well-known ingredients and members as an object for lithium secondary batteries, and manufacture of a lithium secondary battery can be presented with it. The main ingredient or main member is illustrated below.
[0016] As a binder of a Li-Co system multiple oxide, a polytetrafluoroethylene, poly vinylidene fluoride, polyethylene, and ethylene-propylene-diene system polymer etc. is illustrated, and nature, artificial graphites, conductive carbon black, etc., such as a fibrous graphite and scale-like graphite and nodular graphite, are illustrated as an electric conduction agent, for example. The amount of the binder used is per [1] Li-Co system multiple oxide 100 weight section - 10 weight sections extent, especially 2 - 5 weight section extent, and the amount of the electric conduction agent used is per [3] Li-Co system multiple oxide 100 weight section - 15 weight sections extent, especially 4 - 10 weight section extent. Especially especially as a positive-electrode charge collector, an about 30-150-micrometer expanded metal etc. is desirable about 25-300 micrometers in an about 15-50-micrometer foil, a hole vacancy foil, and thickness about 10-100 micrometers in thickness of conductive metals, such as aluminum, an aluminium alloy, and titanium.
[0017] When an example desirable as a negative-electrode active material is given, it is graphites, such as a various kinds of natural-graphites and artificial graphites, for example, fibrous graphite, and scale-like graphite and nodular graphite, and is a polytetrafluoroethylene, poly vinylidene fluoride, polyethylene, and ethylene-propylene-diene system polymer etc. as the binder. The amount of the negative-electrode active material used is per [80] total quantity 100 weight section - 96 weight sections extent of a negative-electrode active material and a binder. Especially especially as a negative-electrode charge collector, an about 25-100-micrometer expanded metal etc. is desirable about 20-300 micrometers in an about 8-50-micrometer foil, a hole vacancy foil, and thickness about 5-100 micrometers in thickness of conductive metals, such as copper, nickel, silver, and SUS.
[0018] As the electrolytic solution, what dissolved salts in the organic solvent is illustrated. As these salts, LiClO4, LiBF4, LiPF6, LiAsF6, LiAlCl4, Li(CF3 SO2)2 N, etc. are illustrated, and those kinds or two sorts or more of mixture is used.
[0019] As an organic solvent, ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, dimethyl sulfoxide, a sulfolane, gamma-butyrolactone, 1, 2-dimethoxyethane, N.N-dimethylformamide, a tetrahydrofuran, 1, 3-dioxolane, 2-methyl tetrahydrofuran, diethylether, etc. are illustrated, and those kinds or two sorts or more of mixture is used. Moreover, 1. is suitable for the concentration of the above-mentioned salts in the electrolytic solution in

about 0.1-3 mols /.
[0020]
[Example] Hereafter, while an example explains this invention to a detail further, the example of a comparison is also given and the remarkable effectiveness of this invention is shown.
[0021] Examples 1-3 and example of comparison 1-5Co 3O4 Li2 CO3 It uses and is Li2 CO3 per Co3 O4 100 weight section. 42 weight sections mixing is carried out, the homogeneous mixture is calcinated at about 980 degrees C for about 10 hours, and it is baking. Obtained massive LiCoO2 Each LiCoO2 of the examples 1-3 which carry out grinding classification, clean ultrasonically using ion exchange water, subsequently heat-treat in atmospheric air, and are shown in Table 1, and the examples 1-5 of a comparison The granular object was obtained. In addition, each LiCoO2 of the examples 1-2 of a comparison About a granular object, above-mentioned rinsing processing and above-mentioned heat treatment have not been performed.
[0022] Each LiCoO2 of an example and the example of a comparison LiCoO2 after the amount of survival of the water solubility [object / granular] lithium compound system impurity after ultrasonic cleaning, heat treatment conditions (temperature and time amount), and heat treatment The total value A of d value of a granular object, specific surface area B, mean particle diameter C, and the value of [(A-11) / (BC)] are shown in Table 1, respectively. In addition, each LiCoO2 of the examples 1-2 of a comparison which has not performed rinsing and heat treatment Each property of a granular object shows the value in the condition that those processings are not performed.
[0023]
[Table 1]

	不純物残存量 wt%	熱処理条件 温度 ℃	熱処理条件 時間 hr	d 値の合計値A (μm)	比表面積B m²/g	平均粒径C (μm)	(A-11) /(BC)	放電容量維持率 %
実施例1	0.0146	500	12	11.1245	0.188	19.5	0.034	93.2
実施例2	0.0101	500	12	11.1368	0.222	18.7	0.033	92.6
実施例3	0.0216	500	12	11.1331	0.194	9.2	0.036	94.0
比較例1	0.1003	-	-	11.1380	0.178	18.2	0.043	83.2
比較例2	0.1091	-	-	11.1387	0.160	18.3	0.047	81.0
比較例3	0.0150	400	12	11.1465	0.189	18.1	0.043	79.2
比較例4	0.0232	900	12	11.1260	0.118	18.4	0.058	74.2
比較例5	0.0241	850	12	11.1230	0.121	18.2	0.056	75.1

[0024] Each LiCoO2 of examples 1-3 and the examples 1-5 of a comparison Using the granular object, the 90 weight section, the polyvinylidene fluoride 7 weight section as a binder, the acetylene black 3 weight section as an electric conduction agent, and the N-

methyl-2-pyrrolidone 70 weight section were mixed, and it considered as the slurry. This slurry is applied on both sides with a thickness [as a charge collector] of 20 micrometers of aluminium foil, it dries, subsequently rolling processing is carried out, and they are 20 mg/cm2 per one side of aluminium foil. The positive-electrode object which has a positive-active-material constituent layer was produced. On the other hand, the scale-like graphite 90 weight section, the polyvinylidene fluoride 10 weight section, and the N-methyl-2-pyrrolidone 200 weight section were mixed, and it considered as the slurry. This slurry is applied to both sides of copper foil with a thickness [as a charge collector] of 14 micrometers, it dries, subsequently rolling processing is carried out, and they are 10.4 mg/cm2 per one side of copper foil. The negative-electrode object which has a negative-electrode active material constituent layer was produced. Next, the positive-electrode object and the negative-electrode object were ****(ed) through the porosity polyethylene separator, and the cylinder can type lithium secondary battery (discharge capacity: 1300mAh) with a height [of 65mm] and an outer diameter of 18mm was manufactured. As the electrolytic solution, it is one mol [per 1l. (the rate of a mixed volume ratio is 3:2:5) of mixed solvents of ethylene carbonate, propylene carbonate, and diethyl carbonate] LiPF6. The solution which comes to dissolve was used and this was sunk in between the above-mentioned positive-electrode object and the negative-electrode object.

[0025] Subsequently, about each lithium secondary battery, the charge-and-discharge cycle property was examined according to the following charge-and-discharge cycle test method, the discharge capacity maintenance factor (%) of a 100 cycle eye was measured, and the result was shown in Table 1.

[Charge-and-discharge cycle test method] Area 1cm2 of a positive-electrode object It is 2 an area of 1cm of charge of 2.5 hours, an after [charge] 1-hour pause, and a positive-electrode object under the constant current and the constant voltage of 4.2V of 2.6mA of hits. Time of terminal voltage being set to 3V under constant current of 1.3mA of hits Discharge capacity (mA-H) is repeatedly computed [by making four processes of pause ** of 1 hour after discharge and discharge into 1 cycle] from the discharge current value in each cycle, and a charging time value 100 times under a room temperature (20 degrees C). Let the rate of the discharge capacity of each cycle eye to a first-time discharge capacity be a discharge capacity maintenance factor (%).

[0026] every of the examples 1-5 of a comparison which have the value of [(A-11) / (BC)] out of range [said formula (1) carried out] from Table 1 -- LiCoO2 Lithium secondary battery using the granular object as positive active material, LiCoO2 of the examples 1-3 with which the value of [(A-11) / (BC)] fills a formula (1) to the discharge capacity maintenance factor in a 100 cycle eye being 85% or less The lithium secondary battery using the granular object as positive active material has 90% or more of high discharge capacity maintenance factor also in a 100 cycle eye, and it turns out that it has the charge-and-discharge cycle property of having carried out the deer and having excelled.

[0027]

[Effect of the Invention] the deer which whose Li-Co system multiple oxide of this invention is useful as positive active material, and was especially excellent in the charge-and-discharge cycle property -- carrying out -- various kinds of objects for electrical

machinery and apparatus -- it is suitable for manufacture of the long lasting lithium secondary batteries for portables etc. above all.